

In: An Introduction to Vanadium  
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## *Chapter 4*

# THE GEOLOGY OF VANADIUM DEPOSITS

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## ABSTRACT

Vanadium is a critical metal for the transition to a low carbon economy but is very rarely extracted from ore deposits as a primary product. Although there are such deposits, vanadium is primarily extracted from vanadiferous titanomagnetite deposits as a co-product with iron. This deposit type is the current dominant worldwide geological source of vanadium. In addition to this there are several other deposits where vanadium has historically or is currently being recovered, either as a by-product (e.g., sandstone hosted uranium deposits) or as a primary product (e.g., vanadate deposits). Carbonaceous shales are also an emerging source for vanadium and can contain substantial tonnages from which vanadium would be extracted as a primary product. The concentration of vanadium within all these geological ore-bodies is strongly controlled by Eh-pH conditions, whether this is from a primary magma such as in layered mafic intrusions and their associated

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titanomagnetite layers, or through remobilisation in supergene settings. This study presents overview data of the current and historical vanadium-bearing orebodies along with their paragenetic implications.

## INTRODUCTION

Vanadium is defined as a critical metal [1] and is one of 14 metals deemed necessary for the transition to a low carbon economy. It's most commonly used as steel hardener or strengthening agent and can be added in small amounts to steel to increase parameters such as castability, rollability and weldability [1]. Vanadium may also be critical for the transition to electric cars, as a component within Li-ion batteries ( $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ ). One of the factors that makes it a critical metal, in terms of supply-chain risks, is the control of vanadium production by a handful of countries, notably China, South Africa and Russia [2]. Brazil has also recently achieved full ramp-up of a new vanadium operation, but this coincided with continual closure of one of the three South-African producers [2].

In terms of modern-day mining, vanadium is recovered as a co-product with iron from vanadiferous titanomagnetite deposits and processed for steel production. It is also recovered as a by-product from sandstone hosted uranium deposits, bauxite, phosphate and carboniferous deposits (e.g., stone coal and crude oil) [2, 3]. In all these deposits, whether as co-product or by-product it generally constitutes less than 2% of the host rock. Historically, vanadium has been processed from numerous other deposit types including vein-hosted Au-V ores (e.g., roscoelite from Stuckslager Mine, USA – [4]), sulfide ore (e.g., Ragra mine, Peru – [5]) and vanadate ore (e.g., Berg Aukas, Namibia – [6]). For the vanadate and sulfide ore bodies vanadium was a primary product but these historical mine sites are now largely exhausted.

## VANADIUM ORE MINERALOGY

Vanadium is usually found as a trace component of minerals, which is a function of the low crustal concentrations (upper crust concentrations of  $\sim 97 \text{ mg kg}^{-1}$ ), and the high Eh-Ph sensitivity [7]. It's most commonly present as a substitution of Fe and Al within other primary and secondary minerals. Owing to the strong correlation with Fe, V is more abundant in mafic rocks [7].

**Table 1. Formula of mining ore grade vanadium minerals**

Mineral	Formula
Bariandite	$\text{Al}_{0.6}(\text{V}^{5+}, \text{V}^{4+})_8\text{O}_{20} \cdot 9\text{H}_2\text{O}$
Carnotite	$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$
Corvusite	$(\text{Na}, \text{K}, \text{Ca}, \text{Mg})_2(\text{V}^{5+}, \text{V}^{4+}, \text{Fe}^{2+})_8\text{O}_{20} \cdot 6-10\text{H}_2\text{O}$
Coulsonite	$\text{FeV}_2\text{O}_4$
Descloizite	$\text{PbZn}(\text{VO}_4)(\text{OH})$
Duttonite	$\text{VO}(\text{OH})_2$
Fernandinite	$(\text{Ca}, \text{K})(\text{V}^{5+}, \text{V}^{4+}, \text{Fe}^{2+})_8\text{O}_{20} \cdot 10\text{H}_2\text{O}$
Hewettite	$\text{CaV}_6\text{O}_{16} \cdot 9\text{H}_2\text{O}$
Melanovanadite	$\text{Ca}(\text{V}^{5+}, \text{V}^{4+})_4\text{O}_{10} \cdot 5\text{H}_2\text{O}$
Minasragrite	$(\text{V}^{4+}, \text{O})(\text{SO}_4) \cdot 5\text{H}_2\text{O}$
Montroseite	$(\text{V}, \text{Fe})\text{O}(\text{OH})$
Mottramite	$\text{PbCu}(\text{VO}_4)(\text{OH})$
Pascoite	$\text{Ca}_3(\text{V}_{10}\text{O}_{28}) \cdot 17\text{H}_2\text{O}$
Patronite	$\text{VS}_4$
Ronneburgite	$\text{K}_2\text{MnV}_4\text{O}_{12}$
Roscoelite	$\text{K}(\text{V}, \text{Al})_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$
Rossite	$\text{Ca}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$
Simplotite	$\text{Ca}(\text{V}_6\text{O}_{16}) \cdot 6\text{H}_2\text{O}$
Sincosite	$\text{CaV}_2\text{O}_2(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$
Stanleyite	$(\text{V}^{4+}, \text{O})(\text{SO}_4) \cdot 6\text{H}_2\text{O}$
Sulvanite	$\text{Cu}_3\text{VS}_4$
Vanadinite	$\text{Pb}_5(\text{VO}_4)_3\text{Cl}$

For minerals where vanadium is a major component there are upwards of 120 mineral species [8, 9], hosted in tetrahedral, pyramidal or octahedral co-ordination [7]. Indeed, in the Evans and White classification scheme, vanadium minerals were subdivided into 12 different groups, including

sulfides, silicates, species with isolated tetrahedral, species with isolated vanadate chains, square-pyramidal  $(VO)^{2+}$  species, uranyl divanadate  $(V_2O_8)^{6-}$  layer complexes, isopoly- and heteropolymolecular complexes, low-valance V-oxyhydroxides, anhydrous oxides, vanadium bronzes, aluminous layer vanadates and other uncertain vanadates [8, 9]. Of these several are, or have been, directly processed as ore minerals [e.g., 4, 5, 10] (Table 1, Figure ), though mostly they are recovered as by-products or co-products within an overall mining operation focused on another metal.

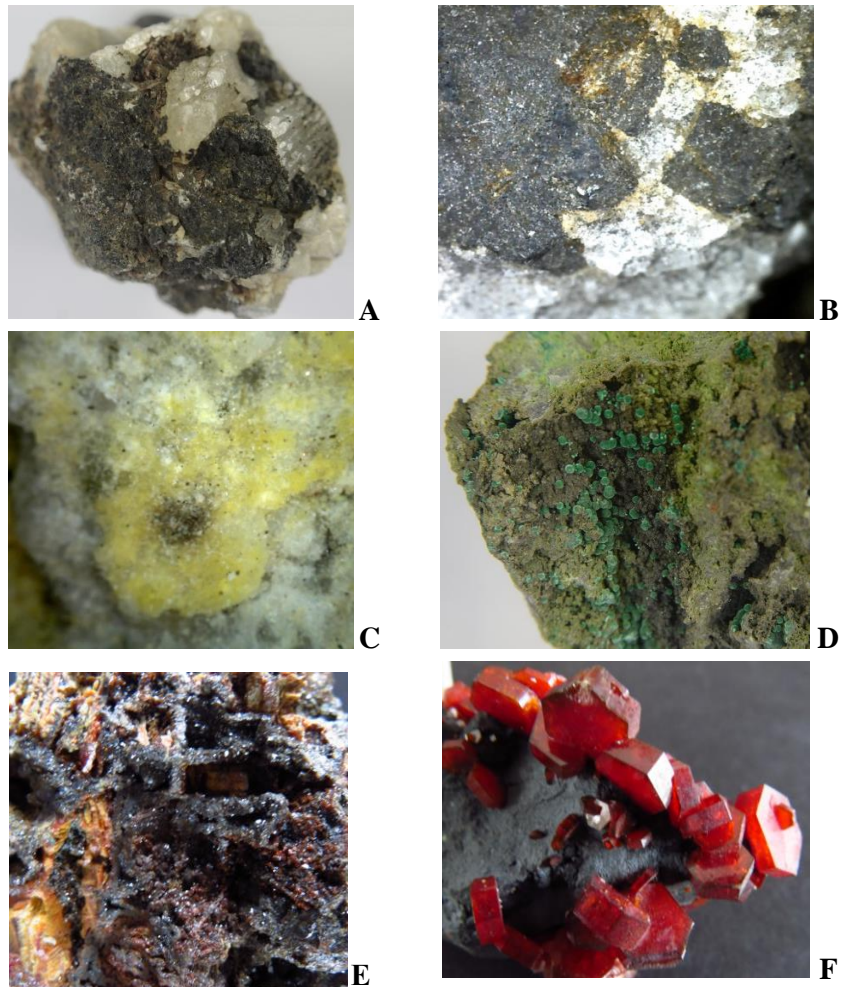


Figure 1. (Continued).

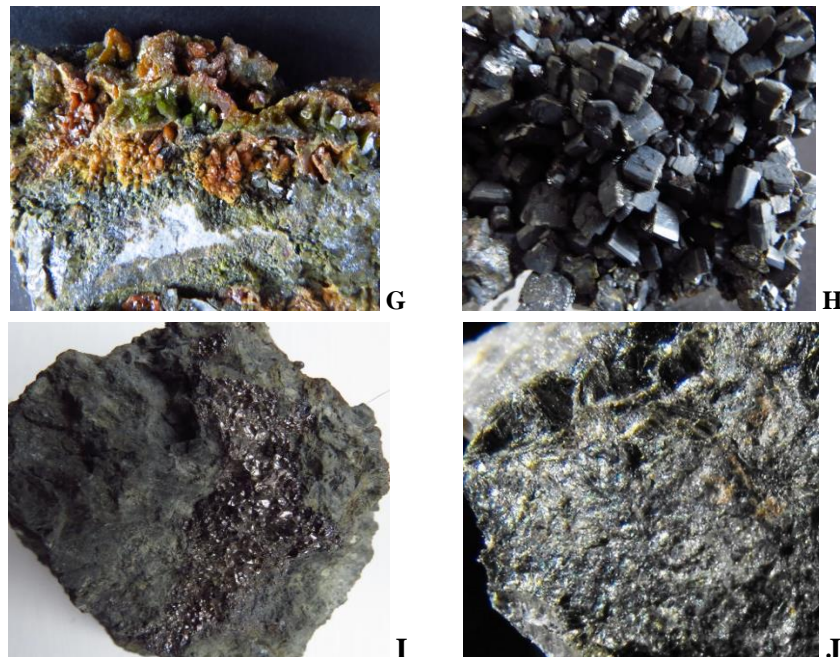


Figure 1. Plates of common vanadium-bearing ore minerals observed within different deposit types. A: Vanadiferous titanomagnetite from Isortoq, Greenland B: Patronite from Cerro De Pasco, Pasco Province, Peru C: Carnotite in calcrete from Klein Trekkopje Trench, Trekkopje Project, Namibia. D: Botryoidal malachite on mottramite from Tsumeb mine, Namibia; E: Vanadinite (red-orange) and descloizite (brown) from the Kabwe deposit, Zambia; F: Vanadinite from the Mibladen mine, Morocco. G: Descloizite (brown) with arsenian descloizite (green) from the Berg Aukas mine, Namibia. H: Descloizite (black) crystals, Berg Aukas mine, Namibia. I: Sulvanite from the Burra Burra mine, Australia. J: Roscoelite (and gold) from the Oriental mine, Allegheny district, California, USA. Specimens and photos (B,D,E,F,G,H,I,J) from the R.J. Bowell collection. Field of view for figure A is 3.5 cm, for figures B,C,E,F,G,H,I,J is 1 cm and for figure D is 2.5 cm.

Vanadium occurs in four principal oxidation states (+2 to +5), although in naturally occurring geological systems this is generally restricted to the range +3 to +5, which covers all the vanadium minerals listed above [e.g., 7, 11].

### Trivalent Vanadium Mineralogy

Minerals containing the trivalent vanadium cation are most commonly seen in soils or through solid-solution replacement of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  in primary and secondary minerals within mafic intrusions. It is from these that vanadium may be recoverable as a by-product. The stability field, in terms of Eh-pH range, for trivalent vanadium minerals is towards the lower end of the Eh range but covering a wide pH range – from acidic to mildly alkaline (Figure ). In soils this is particularly observed in the replacement of  $\text{Fe}^{3+}$  in the mineral goethite ( $\alpha\text{FeOOH}$ ) [12] and the subsequent occasional formation of the vanadium hydroxide montroseite ( $\alpha\text{VOOH}$ ). The substitution of vanadium into goethite displays some complexity in the oxidation state and at low levels the oxidation state may be tetravalent or pentavalent [13], but at high levels of substitution with a peak of up to 13.3 mol% vanadium is substituting as a trivalent cation [13].

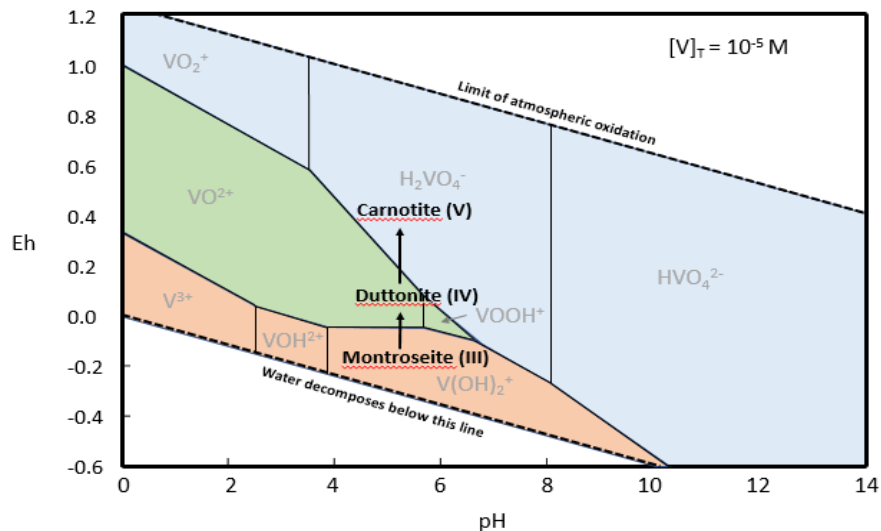


Figure 2. Eh-pH diagram for vanadium, showing the three main valency states and the rough stability zones of three principal vanadium minerals in SSV deposits. Phase diagram derived from [7], with overlying mineral phases from [11].

Other examples of trivalent substitution include: (i) bone coal deposits where vanadium occurs as a solid-solution substitution of  $V^{3+}$  for  $Al^{3+}$  and  $Fe^{3+}$  in micas, tourmaline, garnet, dolomite and aluminosilicate phases [14] and (ii) most notably in vanadiferous titanomagnetite [15]. Indeed the trivalent vanadiferous titanomagnetite host is the principal worldwide vanadium-bearing deposit, and is commonly observed in layered mafic intrusions.

### **Tetravalent and Pentavalent Vanadium Mineralogy**

Along with trivalent vanadium, tetravalent vanadium may also be present in clay minerals, substituting for  $Al^{3+}$  in the octahedral sheet as  $VO^{2+}$  [16]. The stability field, in terms of Eh-pH range, for tetravalent and pentavalent vanadium minerals is towards the upper end of the Eh range but covering a wide pH range. This is particularly the case for pentavalent vanadium minerals which have stability ranges from acidic to alkaline (Figure ). Tetravalent and pentavalent vanadium is the most commonly observed valency in low temperature hydrothermal mineralisation where vanadium ore minerals are precipitating from vanadate-bearing solutions circulating through a suitable host (e.g., karst bodies; [17]). Typical minerals include mottramite, descloizite and vanadinite. Finally, it may also appear in adsorption form which is usually  $V^{4+}$  or  $V^{5+}$ , and particularly easy to recover by simple ion-exchange processing.

## **VANADIUM DEPOSIT TYPES AND IMPLICATIONS FOR PARAGENESIS**

Vanadium mineralisation occurs in four main geological deposits with several other rarer sub-types. The four main deposit types are layered intrusions where vanadium occurs in vanadiferous titanomagnetite deposits, and then three other types where the vanadium is being

concentrated through supergene remobilisation acting in the vadose zone, or near the vadose – phreatic boundary. These three other ore types that host vanadium in extractable quantities are sandstone hosted uranium deposits, carboniferous shale deposits and vanadate deposits. In terms of tonnage the first of these deposits is, by some considerable margin, the dominant geological source of vanadium worldwide. However, it is likely that with the expanding requirements for the metal in a modern economy that more vanadium will need to be sourced from the other geological hosts, particularly the potential host in carboniferous deposits which may also contain substantial tonnages. In addition to these main geological hosts are several other incidental hosts of vanadium that have at times been used to source vanadium. Table 2 and Figure 3 summarise the main worldwide vanadium resources.

### **DEPOSIT 1 – VANADIFEROUS TITANOMAGNETITE (VTM)**

Titaniferous and vanadiferous magnetite deposits are generally known from layered intrusions of which there are several prominent examples, notably;

- i. Bushveld Igneous Complex, South Africa [18, 32].
- ii. Panzhihua V-Ti-Fe ore deposit in Southwest China [19].
- iii. Kachkanar massif in the Ural Mountains, Russia.
- iv. Windimurra Complex in Western Australia [20].
- v. Bell River Complex and the Lac Dore deposit in Quebec, Canada [21].



**Table 2. Table showing deposit type, major vanadium mineral host, prominent deposit examples, vanadium valency states, grades and estimated resources (where known)**

Deposit Type	Major vanadium mineral host	Deposit Example(s)	Valency of major V hosts	Grades (%V <sub>2</sub> O <sub>5</sub> )	Resource (Mt)	References <sup>1</sup>
Vanadiferous titanomagnetite	Vanadiferous titanomagnetite	Bushveld Igneous Complex, South Africa <sup>2</sup>	(III), & minor (IV)	0.6 - 1.9	7400	[18] <i>Bushveld Minerals</i>
		Panzhihua V-Ti-Fe, Southwest China		0.3	3500	[19]
		Windimurra, Western Australia		0.5	235	[20] <i>Atlantic Vanadium Pty Ltd</i>
		Kachkanar massif, Russia		-	-	
		Lac Dore, Quebec, Canada		0.4	120	[21] <i>Vanadiumcorp</i>
		Bell River, Quebec, Canada		0.8	14	<i>Vanadiumcorp</i>
		Isortoq Project, Greenland		0.3	70	<i>Resource 500</i>
		Gabarintha Vanadium Project, Australia		0.7	184	<i>Australian Vanadium</i>
		Barrambie Project, Australia		0.4	280	<i>Neometals</i>
		Mount Peake Vanadium Project, Australia		0.3	160	<i>TNG Limited</i>
		Maracas Menchen Mine, Bahia, Brazil		1.2	38	<i>Largo Resources</i>
		Speewah Vanadium Project, Australia		0.3	4712	<i>King River Resources</i>
		Koitelainen Vosa, Finland		0.1	116	<i>Pursuit Minerals</i>
		Airijoki, Sweden		0.2	44	<i>Pursuit Minerals</i>

<sup>1</sup> Example reference is provided along with any active mining company (as of January 2019). The mining company is in italics, and where present the grade and resource estimate are from their most recent public statements.

<sup>2</sup> Grade and resource estimations for *Bushveld Minerals* include the distinct projects of Makopane, Brits and Vametco. The overall resource tonnage for the Bushveld Igneous Complex includes vanadiferous magnetite occurrences outside of these projects.

**Table 2. (Continued)**

Deposit Type	Major vanadium mineral host	Deposit Example(s)	Valency of major V hosts	Grades (%V <sub>2</sub> O <sub>5</sub> )	Resource (Mt)	References
Uraniferous Deposits	Carnotite, tyuyamunite, corvusite, montroseite, duttonite, simplotite	Colorado Plateau, Utah, Northern Arizona & New Mexico USA <sup>3</sup>	(III), (IV) & (V)	0.1 - 5.0	>5	[22]
		Tonco-Amblayo District, Argentina		0.1 - 0.5	2	[23, 24]
		Amarillo Grande District, Argentina		0.02	24	<i>Blue Sky Uranium Corp</i>
		Karamurun District, Almaty, Kazakhstan		-	-	[23, 24]
		Bigryli Deposit, Northern Territory, Australia		0.1	8	<i>Eclipse Metals Ltd</i>
		Centipede Deposit, Western Australia		-	24	<i>Toro Energy</i>
		Yeelirrie Prospect, Western Australia		-	-	<i>Cameco Australia</i>
Carboniferous Deposits	Montmorillonite, illite, chlorite, roscoelite	Gibellini Shales, Nevada, USA	(III)	0.3	23	[25]; <i>Prophecy Development Corp</i>
		Meade Peak Shale, Wyoming, USA		0.9	4	[26, 60]
		Mecca Quarry Shale, Indiana, USA		0.5	-	[27, 61]
		Doushantuo Formation, Hubei, China		-	-	[28]
		Richmond Project, Toolebuc Formation, Queensland, Australia <sup>4</sup>		0.3	2579	[29]; <i>Intermin Resources Ltd</i>
		Skåne Project, Sweden		0.5	610	<i>Scandivanadium</i>
		Häggån Project, Sweden		0.3	1950	<i>Aura Energy</i>

<sup>3</sup> Resource estimations for these districts are hampered by the substantial numbers of claims (see Figure 3) and the geographical spread. The resource estimation at 5 Mt can be considered an absolute minimum of mined tonnage, relating as it does only to the Slick Rock district in Colorado. For the combination of Colorado, Utah, Northern Arizona and Utah the total resource can be expected to be many times this value.

<sup>4</sup> The Richmond Project resource tonnage is the combination of four distinct prospects in close spatial association. These are the Rothbury prospect (1,764 Mt), Lilyvale prospect (671 Mt), Manfred prospect (96 Mt) and Burwood prospect (48 Mt).

Deposit Type	Major vanadium mineral host	Deposit Example(s)	Valency of major V hosts	Grades (%V <sub>2</sub> O <sub>5</sub> )	Resource (Mt)	References
Carboniferous Deposits	Montmorillonite, illite, chlorite, roscoelite	Green Giant Vanadium Project, Madagascar	(III)	0.7	50	<i>NextSource Materials</i>
Vanadate Ores	Descloizite, mottramite, vanadinite	Otavi Mountainland, Namibia <sup>5</sup>	(IV) & (V)	0.5 - 18	5	[6, 17]
		Kabwe, Zambia		0.6	5.5	[68, 69]
		Mibladen, Morocco <sup>6</sup>		-	-	[70]
		Gallagher deposit, Arizona, USA		-	-	[30]
		Minas do Lueca, Angola		4.0	~1	[31]
Sulfide Ores	Patronite	Ragra Mine, Peru	(V)	-	1 - 10	[5]
Fenitized Feldspathoid Ores	Straczekite, hewettite, duttonite	Potash Sulfur Springs, Arkansas, USA	(III), (IV) & (V)	1.2	4	[71]
Oxide Ores	Montroseite, duttonite <sup>7</sup>	Youanmi Vanadium Project, Australia <sup>8</sup>	(III) & (IV)	0.3	110	[20] <i>Venus Metals</i>

<sup>5</sup> Grade and resource estimations for the Otavi Mountainland vanadate deposits include multiple prospects of which the most significant in terms of tonnage is the Berg Aukas mine.

<sup>6</sup> Tonnage and grades for Mibladen may not be extensive, but the resource is included due to the world class vanadinite specimens, particularly from the Coud'a workings.

<sup>7</sup> The mineralogy of the deposit hasn't been reported yet but is presumed to be vanadium-bearing oxides similar to those observed in uraniferous deposits, but without any association with uranium.

<sup>8</sup> The Youanmi vanadium project is unusual as it results from deeply weathered and highly oxidised vanadiferous titanomagnetite. As such it contains quite distinct mineralogy compared with traditional hard-rock vanadiferous titanomagnetite deposits and is therefore recorded separately. The process of weathering and oxidation means that processing may be possible through simple leaching, with the co-extraction of Ni, Cu and Co.

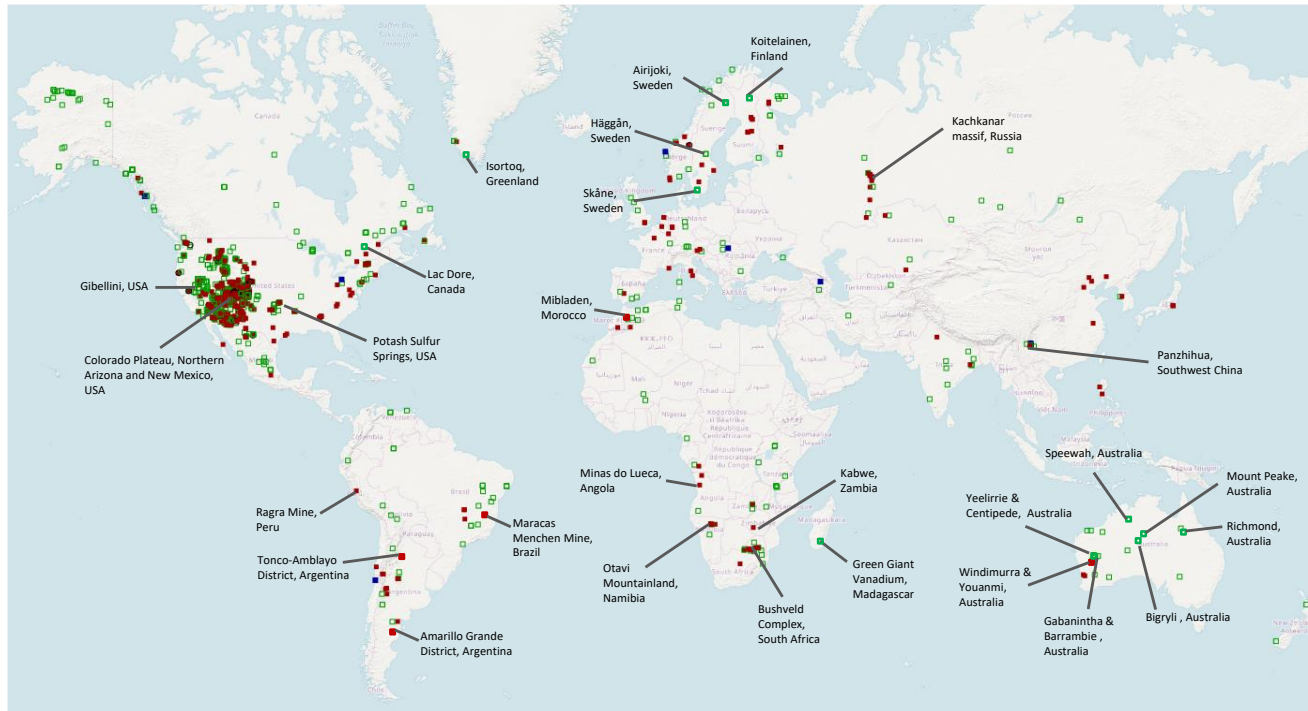


Figure 3. Deposit map of the world showing all the mines that have produced vanadium (red), and all prospects that have, or are being explored for vanadium (green). Key processing plants are marked in blue. Locations are based on the USGS mineral resources data system (<https://mrdata.usgs.gov/mrds/>). This map has been updated to include recent prospects. As part of the MRDS database ferrovanadium plants are also in red and a lot of the occurrences in Europe refer to these ferrovanadium plants rather than mines.

The stratigraphy of these layered deposits shows substantial similarities with the vanadiferous magnetite layers occurring in the upper zone of many of these (Figure ). However, this is not always the case, as observed in the Panzhihua V-Ti-Fe oxide ores which are dominantly hosted in the lower zones of the intrusion [19]. This difference may relate to a different evolution of the primitive magmas that fed the intrusions. It is notable, for example, that the complete layered sequence observed in the Bushveld Complex and the Windimurra Complex begins with the early fractionation of chromite and chromitite layers in the Lower Zone, followed in due course by magnetite in the Upper Zone (e.g., [33]). The crystallization of chromite and then magnetite from silicate magmas is related to the  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratio of the liquid and this is dependent upon temperature, water content and  $f\text{O}_2$  [19, 32]. The  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratio of the magma is increased when Fe-poor phases (e.g., plagioclase) and FeO-bearing phases (e.g., olivine) crystallize out. As these are anhydrous this also reduces the water content. In this way fractional crystallization initially leads to the crystallization chromite and then subsequently magnetite later in the sequence [33, 34]. The absence of chromite from the Panzhihua sequence may relate to the early fractionation and loss of an ultramafic portion of the primitive magma [19], whilst its absence from the Lac Dore Complex and Bell River Complex is thought to be related to a hypothetical hidden zone [21].

Fractional crystallization in this regard explains the crystallization of disseminated magnetite, however the magnetite forming in the Panzhihua intrusion frequently occurs as layers enclosing, or infiltrating previously crystallized silicate minerals [19]. Furthermore, there are still some challenges in explaining how monomineralic magnetite layers can form on the scale observed in complexes such as the Bushveld. Evidence from Sr-isotope variation, for example, does not support the suggestion that repetitive injections of fresh magma are part of the explanation [18]. It is possible that mineral settling plays a crucial role, which is supported by the graded upper contacts in the Bushveld Complex [18], whereas within Panzhihua, the particular textures observed suggest that the magnetite-rich layers are crystallizing from a fractionated Fe-rich melt, which owing to its

relative high density has sunk and accumulated as a stagnant layer towards the base of the present chamber [19]. The formation and final crystallization of this immiscible Fe-rich melt may also be being controlled by variations in oxygen fugacity and pressure, which in turn may assist in the monomineralic crystallization of magnetite.

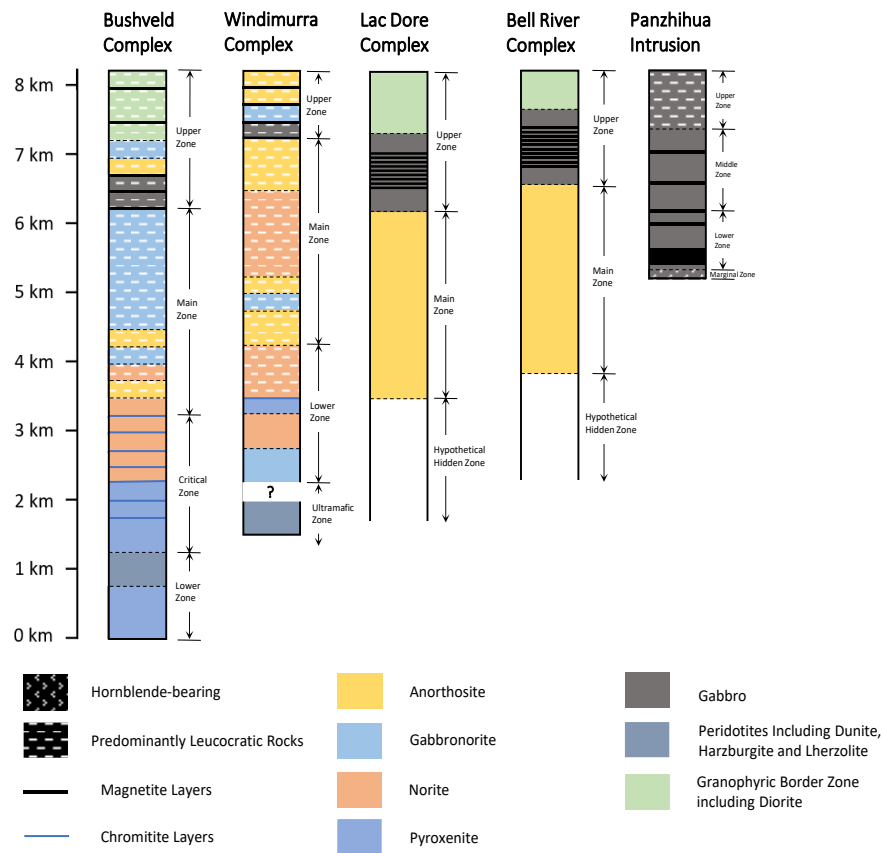


Figure 4. Comparison of the schematic stratigraphic column of the Bushveld Complex, Windimurra, Lac Dore and Bell River Complexes, and Panzhihua intrusion (modified from 19, 20, 21).

Vanadiferous magnetite deposits are responsible for nearly a quarter of the global vanadium production and typically have overall grades in the region of 0.1 - 1%  $V_2O_5$  [18]. The vanadium content of vanadiferous

magnetite has an upper limit of roughly 1.4 wt% [18], which is dependent upon the vanadium concentration of evolved basic magmas (~400 ppm) and the partition coefficient. This ranges from 7 to 35 [35] depending on the  $f_{O_2}$ . Therefore, in a layered intrusion setting, the first magnetite to form will have a vanadium content of 1.4 wt%, after which subsequent magnetite deposition will be crystallizing from progressively depleted magma, therefore producing progressively depleted vanadiferous magnetite [18, 21]. This is particularly well observed in the Bushveld Complex where the vanadium content of the magnetite layers starts initially at 1.3 wt%, before decreasing to 0.2 wt% nearer the roof of the intrusion [36].

## **DEPOSIT 2 – SANDSTONE-HOSTED URANIUM DEPOSITS (SSV)**

SSV deposits have been identified in all continents, and many are known to have high contents of vanadium [24]. These deposits of vanadium - and uranium-bearing sandstone (known as sandstone-hosted vanadium [SSV] deposits) have average resource and ore grades that range from 0.1 to 1 wt% vanadium. On a global scale, the United States has been and is currently the main producer of vanadium from SSV deposits, particularly from those on the Colorado Plateau. Additionally, these SSV deposits are the chief domestic source of vanadium in the United States [37, 38, 39, 40]. Example SSV deposits include;

- i. Western Colorado, Eastern Utah, Northern Arizona and New Mexico [22].
- ii. Bigrlyi deposit in Northern Territory, Australia.
- iii. Tonco-Amblayo district in Argentina.
- iv. Amarillo Grande district in Argentina.
- v. Karamurun district of Almaty Oblasy, Kazakhstan [24].

One of the original simplifications proposed by the early miners was to consider two main types of vanadium-bearing SSV ore, namely “roscoelite

ore” and “carnotite ore” [11]. Although this is highly over simplistic it highlights the prominence of vanadium silicate ore, where vanadium was extracted for itself (e.g., in the Uravan mineral belt – [41], or the Slick Rock District, Colorado – [22]) and oxide-vanadate ores where vanadium was extracted as a by-product of uranium mining. For vanadium mining in America the principal mineral hosts were a mixed vanadium silicate-montmorillonite clay, with minor roscoelite (except at Placerville where it dominated) and vanadium-bearing chlorite [11].

The commercial beneficiation of vanadium as a by-product from uraniferous deposits is generally restricted to “carnotite ore”, which since its original inception as a term by early miners has become highly complex. Indeed, in SSV ores there are more than 40 different V-bearing minerals, though many of these are very rare. Vanadium-bearing uranium minerals derive from redox weathering of reduced V and U minerals and can produce extensive roll-front type deposits [7, 11]. The primary vanadium-bearing mineral formed during redox weathering is carnotite, and carnotite related variants such as tyuyamunite. However, as there are a wide range of reduction potentials and pH conditions during formation there are correspondingly a range of vanadium minerals depending on whether the conditions are highly reducing (i.e., +3 valency), or highly oxidising (i.e., +5 valency). For reducing conditions at largely neutral pH the ores are characterised by a black mineral suite consisting of coffinite and uraninite, along with the vanadium-bearing minerals montroseite, duttonite and simplotite [42]. In conditions that are more oxidising and acidic the resultant vanadium-bearing minerals become carnotite, corvusite, tyuyamunite and hewettite [42, 43, 44].

The formation of uranium-vanadium ore bodies follows two main forms, namely tabular or roll-front deposits (Figure). There is an additional association of vanadium with calcrete hosted surficial uranium-vanadium deposits [45]. The tabular and roll-front deposits of the Colorado Plateau are often continuous with one another and are interpreted to have formed through the same essential process [22]. There are numerous mines that have exploited these deposits (Figure 3), and the general mineralised area can be observed to spread between four US states (Colorado, Utah,



Arizona and New Mexico). The process of concentration can be summarised as the deposition of uranium-vanadium bodies at the interface between oxidising and reducing solutions [22]. The vanadium on the Colorado plateau deposits tends to be concentrated towards the oxidised side of the uranium-bearing interface [22].

Although average grades are generally in the range of 0.1 to 1.0 wt%, vanadium concentrations in SSV ores (expressed as  $V_2O_5$ ) can be greater than 1 wt%, and, for example, some deposits in southwestern Colorado have grades of more than 2.5% [22]. However, most are less than this as seen by the Bigrlyi deposit in Northern Territory, Australia which has a grade of 0.12 weight % and Tonco-Amblayo district in Argentina, which had grades ranging from 0.1 (at the Don Otto mine) to 0.5 weight % (at the Los Berthos mine) vanadium [24]. Roscoelite ores, as mentioned briefly in SSV ores, are a sub-class of these roll-front uranium deposits where vanadium has been preferentially concentrated, with only subordinate uranium.

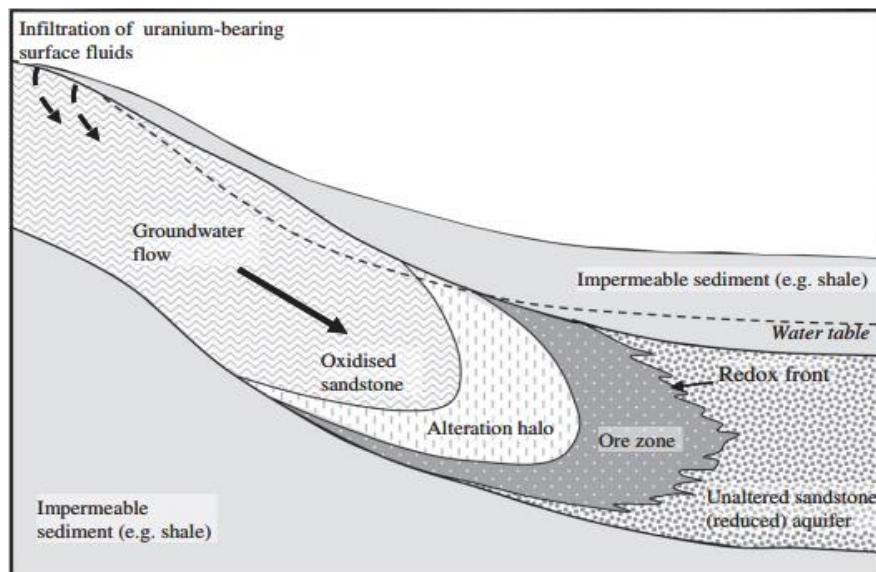


Figure 5. A generalised conceptual model for a roll-front deposit. Taken from [45], and references therein. Vanadium concentrates with uranium in the ore-zone at the interface between the limit of oxidation and reduction.

### **DEPOSIT 3 – CARBONIFEROUS DEPOSITS**

Elevated vanadium concentrations are associated with three main types of carboniferous deposits including crude oil, coal deposits and carbonaceous shales. Of these the carbonaceous shales are considered the most prospective as a potential source of vanadium, and can carry substantial tonnages (Table 2).

Crude oils commonly contain elevated concentrations of numerous transition metals, particularly including V, Ni and Mo [46, 47, 48]. Within crude oil especially the vanadium tends to concentrate into the heavy crude fractions, a process that is enhanced by the presence of reduced sulfur species [49]. The concentrations of vanadium in these crude oil deposits may reach 1200 ppm [50], and in the asphaltene portions this may reach up to 5000 ppm [51]. Vanadium has a number of pathways into the hydrosphere, and from there into crude oils. In particular, sources for vanadium can come from continental weathering, hydrothermal vent systems and volcanic ash [52]. In moderately reducing environments (0.5 to -0.2 Eh Volts) where carboniferous deposits are deposited, vanadium mainly occurs as a vanadyl ( $\text{VO}^{2+}$ ) ions, and under normal pH conditions becomes readily hydrolysed and adsorbs on to humic acids and porphyrins to form stable complexes [53]. Crude oil may also become enriched in vanadium post-formation through interaction with microscopic vanadium-rich inclusions in the oil (e.g., brines), or through direct scavenging from the bedrock via fluid-rock, oil-rock or oil-fluid interactions [48].

In coal deposits it doesn't tend to be the coal itself that hosts the vanadium, as this is typically present in concentrations less than 100 mg  $\text{kg}^{-1}$  [54]. Instead the vanadium is mainly found in the interleaved non-carbonaceous minerals, typically clays, that bulk out the coal deposit. The most prospective coal deposits for associated vanadium extraction are therefore those with high organic, or aluminosilicate content. Concentrations in clay minerals within the coal deposits have been recorded up to 420 mg  $\text{kg}^{-1}$  [55].

Metalliferous carbonaceous shales occur primarily in late Proterozoic and Phanerozoic marine successions. The term shale is used here broadly

to include a range of carbonaceous rocks that include marls and mudstones. These fine-grained sedimentary rocks were deposited in epeiric (inland) seas and on continental margins. They typically contain high concentrations of organic matter (greater than 5%) and reduced sulfur (greater than 1%; mainly as pyrite), as well as a suite of metals, such as copper, molybdenum, nickel, PGEs, silver, uranium, vanadium, and zinc [e.g., 25, 56, 57, 58, 59]. Concentrations regularly exceed 0.18%  $V_2O_5$  and can be as high as 1.7%  $V_2O_5$ . As with coal deposits this vanadium is typically hosted in the interleaved clay minerals. There are several well characterised vanadiferous carboniferous shales which include:

- i. Gibellini shales, Elko, Nevada [25].
- ii. Meade Peak Phosphatic Shale Member of the Phosphoria Formation in Idaho and Wyoming [26, 60].
- iii. Portions of the Toolebuc Formation in Queensland, Australia [29].
- iv. Skåne Project, Sweden
- v. Häggån Project, Sweden

The concentration of vanadium in the Toolebuc formation is assumed to be indicative of the general concentration process within carbonaceous shales. In this formation [29] make the general observation, in accordance with previous work, that vanadium was most likely accumulated by marine organisms (e.g., plankton) and deposited in the sediment as part of the total organic carbon content. However, the process of compaction and diagenesis has resulted in the collapse of the organic carbon structures and the mobilisation of this vanadium, which is then free to bond to other phases. The current hypothesis is that this vanadium bonds preferentially to mixed layer clays such as illite or montmorillonite.

Although these black shales have long been recognised as potential sources of vanadium, they are not frequently exploited. Project development is underway at the Gibellini vanadium prospect in Nevada (Woodruff Formation), and if production begins, it will be the first primary shale-hosted producer of vanadium in the United States. The Julia Creek deposit (Toolebuc Formation) is also in the planning stages. The Green

Giant deposit in southern Madagascar (Energizer Resources, Inc., 2013), Skåne Project, Sweden (Scandivanadium) and Häggån Project, Sweden (Aura Energy) all represent other potential shale projects that may come on line in the coming years. Furthermore, vanadium is produced in large quantities from carboniferous deposits in China, particularly in bone coal and carbonaceous shale [14]. Taken together, this all suggests that vanadium may be increasingly sourced from carbonaceous deposits in addition to the traditional major host in vanadiferous titanomagnetite deposits.

#### **DEPOSIT 4 – VANADATE ORES**

Vanadate ores are particularly prominent in parts of Southern Africa, specifically Namibia [6, 17], Zambia [62] and Angola [31]. Although now largely mined out, these deposits did once contain several million tonnes of ore [7, 17]. Examples such as Berg Aukas and Abenab from Namibia are stratabound base metal sulfide deposits in carbonate host rocks that also contain an overprint of secondary vanadium minerals as vanadates (chiefly descloizite, vanadinite and mottramite). It is hypothesized that these deposits may have formed through supergene oxidation of vanadium rich shales and base metal sulfides forming in paleokarst landscapes. The tonnage of these deposits was generally low but the grades could be very high, reaching up to 18.75% (e.g., Uris; [17]).

Base metal-precious metal deposits in volcanic terrains in western US/Northern Mexico, may also commonly contain vanadium minerals in the supergene zone with some (e.g., Gallagher Vanadium deposit, [30]) reaching up to 0.5-1 wt%  $V_2O_5$  in the oxidized ore and often associated with anomalous uranium and molybdenum as well).

Prominent examples of vanadate-bearing ores include:

- i. Otavi Mountainland (e.g., Berg Aukas) [17].
- ii. Kabwe, Zambia [68, 69].
- iii. Mibladen, Morocco [70].

From the literature, it is possible to suggest a general paragenesis for the formation of these deposit types related to the replacement of pre-existing carbonate formations. Structural controls consist primarily of fractures within hosting carbonates that allow for the free circulation of vanadium-bearing solutions. As such most deposits occur in the supergene environment, in zones with extensive brittle faulting (e.g., [17]). The largest deposits represent locations where several structural lineaments intersect allowing for intense brecciation, pipe collapse and intense karstic dissolution. [17] recognise two sub-types consisting of (i) breccia filled deep pipes and veins located along structural lineaments (e.g., Figure ) and (ii) “sand sacks” which consist of carbonate-vanadate cemented debris filling karstic cavities (Figure 7).

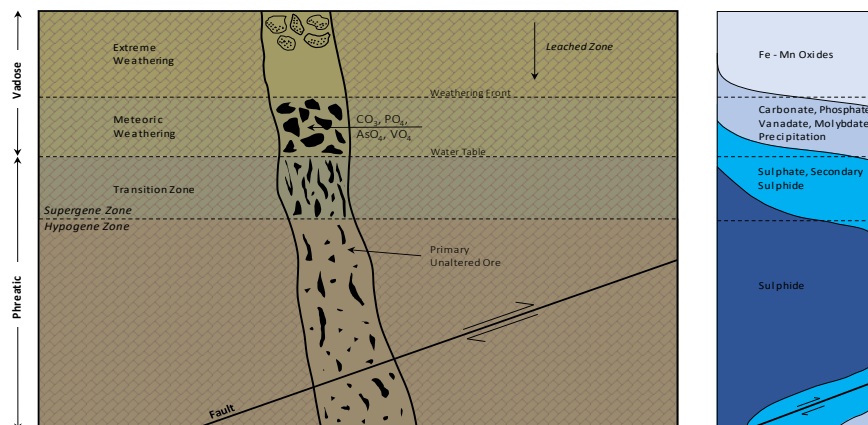


Figure 6. Schematic image showing the formation of vanadate ores within the meteoric zone of a linear ore body cutting through host limestone. The ore-body may be fault-bounded breccias or cross-cutting sulfide-rich ore-bodies, usually hosted in karstic geological terranes (Modified from figures in [17] & [30]).

Generally, vanadium is thought to be sourced from siliciclastic country rocks or mafic basement lithologies before combining with other base metals released from the oxidation of primary sulfide deposits. The acidity from these oxidising sulfides, coupled with low Eh conditions near the boundary between the phreatic and vadose zone in a karst network represent very favourable conditions for vanadate mineral precipitation.

This would especially be the case if there was abundant organic matter to keep the Eh conditions low [17].

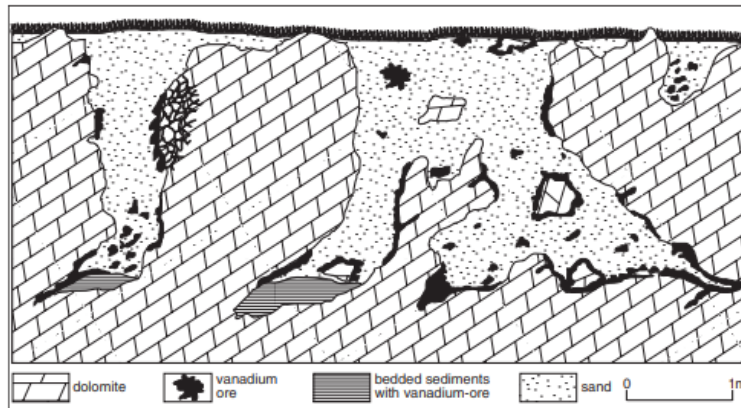


Figure 7. Sand sacks vanadate ore within a paleokarst landscape (Taken from [17] and references therein).

## DEPOSIT 5 – OTHER VANADIUM SOURCES

Patronite ( $VS_4$ ) has been recovered as a primary product from sulphidic ore in Peru since 1905. The mining operation to recover this vanadium remained active until 1955 until the supply was largely exhausted [10]. Vanadium concentrations in other massive sulfide ore bodies have also been identified from the Vihanti Massive Sulfide base-metal deposit in Finland.

Some magmatic-hydrothermal niobium-titanium deposits contain elevated concentrations of vanadium. Deposits at Potash Sulfur Springs (also called Wilson Springs) in Arkansas were the most important sources of vanadium in North America in the 1970s and 1980s, and nearly 4.3 million metric tons of 1.2%  $V_2O_5$  were produced. By 1990, all the mines at Wilson Springs were closed.

Bauxite residues often contain vanadium concentrations (1.2 – 15.6 mg/l) that need to be extracted and removed as being either a penalty element, or potential source of toxicity. As such, removal and recovery of

vanadium from these residues represents a source of vanadium ([63] and references therein).

Phosphorite deposits are known to contain vanadium, which is often used as a pathfinder for low uranium concentrations as well. A good example is the phosphorite member of the Eshidiyya basin in Southern Jordan which was observed to contain between 50 and 484 ppm vanadium in certain stratigraphic units [64], and the phosphorite beds in Idaho which averaged 0.14 wt%  $V_2O_5$  [65]. As with bauxite residues the extraction of vanadium as a by-product follows from the initial leaching process.

Although not a geological deposit, anthropogenic vanadium represents a significant source of vanadium, principally through the reprocessing of vanadium-bearing slag, itself a by-product of the smelting of iron ores. Concentrations of vanadium pentoxide in these slags can reach 12 – 24% [66] and, for example, slag reprocessing represents 40% of the vanadium output of China [67].

## CONCLUSION

The increasing importance of vanadium to the modern economy means that sources of vanadium for extraction will be sought from a variety of deposit types. The historic and currently significant deposits will likely remain, particularly the layered vanadiferous titanomagnetite deposits and to some extent the sandstone hosted uranium ores. However, it is likely that new deposit types such as carbonaceous shales will become increasingly important, especially given the substantial tonnages that are contained within them. In that context the paragenesis of all these vanadium-bearing deposits has important implications for exploration and in particular the strong Eh-Ph control on vanadium precipitation. The vanadium in the vanadiferous titanomagnetite is nearly unique amongst geological sources of vanadium in precipitating direct from the magma. For all the other potential geological sources of vanadium the concentration process is occurring during meteoric weathering within the vadose and vadose-phreatic zone, or through the process of diagenesis and

compaction which releases vanadium from organic matter trapped in sediments. In vanadate and to some extent sandstone hosted uranium deposits the vanadium is being remobilised during redox reactions (from original trace hosts in siliciclastic sediments or mafic basement material), before precipitating at redox boundaries, often in the presence of a strongly reducing agent such as organic matter. This strong Eh control on the precipitation of vanadium explains the strong association with uranium in roll-front type deposits as well as within the vanadate deposits present in paleokarst settings. In the same way the host in carbonaceous shale is controlled by the presence of organic matter in the depositing shales, although the final concentration is completed through the process of diagenesis and adsorption of mobile vanadium on to illite-montmorillonite mixed clays. The association of vanadium concentrations with these redox boundaries, particularly in zones with high levels of organic matter can be used as an exploration tool for new vanadium-bearing deposits.

## REFERENCES

- [1] Moss, R., Tzimas, E., Kara, H., Willis, P., Kooroshy, J. (2011): *Critical Metals in Strategic Energy Technologies – assessing rare metals as supply-chain bottlenecks in low-carbon energy technologies*. Publications Office of the European Union, p. 164.
- [2] U.S. Geological Survey, 2018, *Mineral commodity summaries*: U.S. Geological, p.200, <https://doi.org/10.3133/70194932>.
- [3] Kelley, K.D., Scott, C.T., Polyak, D.E., Kimball, B.E. (2017): Vanadium. In: Schulz, K.J., DeYoung, J.H., Seal II, R.R. & Bradley, D.C. (Eds): *Critical Mineral Resources of the United States – Economic and Environmental Geology and Prospect for Future Supply* (Chapter U). U.S. Geological Service, Professional Paper 1802-U: U1-U36.
- [4] Clark, W.B. & Carlson, D.W. (1956) Mines and mineral resources of El Dorado County, California. *California Journal of Mines and Geology* (Report 52): 52(4): 426, 533, Pl. 10.



- [5] Hewett, D.F. (1909): *Vanadium deposits in Peru, American Institute of mining engineers (A.I.M.E.) Transaction*: 40:274.
- [6] Misiewicz, J.E. (1988): *The Geology and Metallogeny of the Otavi Mountain Land, Damara Orogen, SWA/Namibia, with particular reference to the Berg Aukas Zn-Pb-V Deposit – A model of Ore Genesis* Master of Science Thesis, Johannesburg. 130p.
- [7] Huang, J-H, Huang, F., Evans, L. & Glasauer, S. (2015): Vanadium: Global (bio)geochemistry. *Chemical Geology*, 417, pp 68-89.
- [8] Evans, H.T. & White, J.D. (1987): The colourful vanadium minerals. *Mineral. Rec.*, 18, pp 333-340.
- [9] Schindler, M. & Hawthorne, F.C. (2000): A crystal-chemical approach to the composition and occurrence of vanadium minerals. *The Canadian Mineralogist*, 38, pp 1443 – 1456.
- [10] Moskalyk, R.R. & Alfantazi, A.M. (2003): Processing of vanadium: a review. *Minerals Engineering*, 16 (9), pp 793 – 805.
- [11] Weeks, A.D. (1961): Mineralogy and geochemistry of vanadium in the Colorado plateau. *J. Less-Common Metals*, 3, pp 443-450.
- [12] Schwertmann, U. & Pfab, G. (1994): Structural vanadium in synthetic goethite. *Geochimica Cosmochimica Acta*, 58 (20), pp 4349-4352.
- [13] Vodyanitskii, Y.N. (2013): Determination of the oxidation states of metals and metalloids: An analytical review. *Eurasian Soil Science*, 46, pp 1139-1149.
- [14] Xiao, W.D., Yang, X. & Zhang, P. (2010): Study of process mineralogy for hydrometallurgical extraction of vanadium and aluminium from bone coal. *Minerals and Metallurgical Processing*, 32 (3), pp 155 – 160.
- [15] Balan, E., De Villiers, J.P.R., Eeckhout, S.G., Glatzel, P., Toplis, M.J., Fritsch, E., Allard, T., Galois, L. & Calas, G. (2006): The oxidation state of vanadium in titanomagnetite from layered basic intrusions. *American Mineralogist*, 91 (5-6), pp 953-956.
- [16] Gehring, A.U., Fry, V., Luster, J. & Sposito, G. (1993): The chemical form of vanadium (IV) in kaolinite. *Clay Mineralogy*. 41 (6), pp 662-667.

- [17] Boni, M., Terracciano, R., Evans, N.J., Laukamp, C., Schneider, J. & Bechstadt, T. (2007): Genesis of vanadium ores in the Otavi mountainland, Namibia. *Economic Geology*, 102(3), pp 441-469.
- [18] Cawthorn, R.G., Barnes, S.J., Ballhaus, C., & Malitech, K.N. (2005): Platinum Group Element, Chromium and Vanadium Deposits in Mafic and Ultramafic Rocks. *In: Economic Geology one hundredth anniversary volume*, Chapter 8, pp. 215-249.
- [19] Zhou, M.-F., Robinson, P.T., Leshner, C.M., Keays, R.R., Zhang, C.-J. & Malpas, J. (2005): Geochemistry, petrogenesis and metallogenesis of the Panzhihua gabbroic layered intrusion and associated Fe-Ti-V oxide deposits, Sichuan Province, SW China: *Journal of Petrology*, 46 (11), pp 2253-2280.
- [20] Ivanic, T.J., Wingate, M.T.D., Kirkland, C.L., Van Kranendonk, M.J. and Wyche, S. (2010): Age and significance of voluminous mafic-ultramafic magmatic events in the Murchison domain, Yilgarn Craton: *Australian Journal of Earth Sciences*, 57 (5), pp 597-614.
- [21] Taner, M.F., Ercit, T.S. & Gault, R.A. (1998): Vanadium-bearing magnetite from the Matagami and Chibougamau mining districts, Abitibi, Quebec, Canada: *Exploration and Mining Geology*, 7 (4), pp 299-311.
- [22] Shawe, D.R., 2011, Uranium-vanadium deposits of the Slick Rock district, Colorado: *U.S. Geological Survey Professional Paper 576-F*, 67, 20 p.
- [23] Dahlkamp, F.J. (2009): *Uranium deposits of the world—Asia*: Berlin, Germany, Springer-Verlag, 945 p.
- [24] Dahlkamp, F.J. (2010): *Uranium deposits of the world—USA and Latin America*: Berlin, Germany, Springer-Verlag, 423 p.
- [25] Desborough, G.A., Poole, F.G., Hose, R.K. & Radtke, A.S. (1979): *Metals in Devonian kerogenous marine strata at Gibellini and Bisoni properties in southern Fish Creek Range*, Eureka County, Nevada: U.S. Geological Survey Open-File Report 79-530, 31 p.
- [26] McKelvey, V.E., Strobell, J.D., Jr., & Slaughter, A.L. (1986): The vanadiferous zone of the Phosphoria Formation in western Wyoming

and Southeastern Idaho: *U.S. Geological Survey Professional Paper* 1465, 27 p. 2.

- [27] Coveney, R.M., Jr., and Martin, S.P. (1983): Molybdenum and other heavy metals of the Mecca Quarry and Logan Quarry shales: *Economic Geology*, 78, pp. 132–149.
- [28] Delian, F., Jie, Ye, & Tiebing, Lui, (1992): Black shale series-hosted silver-vanadium deposits of the Upper Sinian Doushantuo Formation, western Hubei Province, China: *Exploration and Mining Geology*, 1 (1), pp. 29–38.
- [29] Lewis, S.E., Henderson, R.A., Dickens, G.R., Shields, G.A., & Coxhell, S. (2010): The geochemistry of primary and weathered oil shale and coquina across the Julia Creek vanadium deposit (Queensland, Australia): *Mineralium Deposita*, 45 (6), pp. 599–620.
- [30] Bowell, R., Luetcke, R. & Luetcke, M.R. (2016): Mineralogy of the Gallagher Vanadium Property and Manila Mine Cochise County, Arizona. *Rocks and minerals*, 90, pp 338-348.
- [31] Millman, A.P. (1960): The descloizite-mottramite series of vanadates from minas-do-lueca, Angola. *American Mineralogist*, 45 (7-8), pp 763-773.
- [32] Reynolds, I.M. (1985): The nature and origin of titaniferous magnetite-rich layers in the upper zone of the Bushveld Complex – A review and synthesis: *Economic Geology*, 80, pp 1089-1108.
- [33] Irvine, T.N. (1975): Crystallization sequences in Muskox intrusion and other layered intrusions. 2. Origin of chromitite layers and similar deposits of other magmatic ores. *Geochimica et Cosmochimica Acta*, 39, p991-1020.
- [34] Wilson, M. (1989): *Igneous Petrogenesis*. London, Unwin Hyman. 494 p.
- [35] Toplis, M.J. & Corgne, A. (2002): An experimental study of element partitioning between magnetite, Clinopyroxene and iron-bearing silicate liquids with particular emphasis on vanadium. *Contributions to Mineralogy and Petrology*, 144, pp 22-37.
- [36] Molyneux, T.G. (1970): The geology of the area in the vicinity of Magnet Heights, Eastern Transvaal, with special reference to the

- magnetic iron ore. *Geological Society of South Africa, Special Publication*, 1, pp 228-241.
- [37] Fischer, R.P. (1968): The uranium and vanadium deposits of the Colorado Plateau region, in Ridge, J.D., ed., *Ore deposits of the United States, 1933–1967*: New York, N.Y., American Institute of Mining, Metallurgical, and Petroleum Engineers, v. 1, p. 735–746.
- [38] Fischer, R.P. (1973): Vanadium, in Brobst, D.A., and Pratt, W.P., eds., *United States mineral resources: U.S. Geological Survey Professional Paper 820*, p. 679–688, accessed January 1, 2013, at <http://pubs.er.usgs.gov/publication/pp820>.
- [39] Polyak, D.E. (2012): Vanadium, in *Metals and minerals: U.S. Geological Survey Minerals Yearbook 2011*, v. I, p. 80.1–80.9.
- [40] Polyak, D.E. (2013): Vanadium: U.S. Geological Survey Mineral Commodity Summaries 2013, p. 178–179.
- [41] Fischer, R.P. & Hilpert, L.S. (1952): Geology of the Uravan mineral belt. *U.S. Geol. Survey. Bull.* 988-A, pp 1-13.
- [42] Roach, C.H. & Thompson, M.E. (1959): Sedimentary structures and localization and oxidation of ore at the Peanut Mine, Montrose County, Colorado. *U.S. Geological Survey. Prof. Pap.* 320, pp 197-202.
- [43] Elston, D.P. & Botinelly, T. (1959): Geology and mineralogy of the J.J. mine, Montrose county, Colorado, *U.S. Geol. Surv. Prof. Pap.* 320, pp 203-212.
- [44] Weeks, A.D., Coleman, R.G. & Thompson, M.E. (1959): Summary of the ore mineralogy, part 5 of Garrels, R.M., and Larsen, E.S., III, comps., *Geochemistry and mineralogy of the Colorado Plateau uranium ores (3d ed.)*: U.S. Geological Survey Professional Paper 320, p. 65–79.
- [45] Pownceby, M.I. & Johnson, C. (2014): Geometallurgy of Australian uranium deposits. *Ore Geology Reviews*, 56, pp 25-44.
- [46] Aleshin, G.N., Altukhova, Z.P., Antipenko, V.R., Marchenko, S.P. & Kamyaynov, V.F. (1984): Distribution of vanadium and vanadyl porphyrins in petroleum distillates of different chemical types. *Petrol. Chem.* 24, pp 191-195.

- [47] Amorim, F.A.C., Welz, B., Costa, A.C.S., Lepric, F.G., Vale, M.G.R. & Ferreira, S.L.C. (2007): Determination of vanadium in petroleum products using atomic spectrometric techniques. *Talanta*, 72, pp 349-359.
- [48] Ventura, G.T., Gall, L., Siebert, C., Prytulak, J., Szatmari, P., Hurlimann, M. & Halliday, A.N. (2015): The stable isotope composition of vanadium, nickel and molybdenum in crude oils. *Applied Geochemistry*, 59, pp 104-117.
- [49] Punanova, S.A. (2014): Supergene transformed naphthides: peculiarities of trace-element composition. *Geochem. Int.* 52 (1), pp 57-67.
- [50] López, L. & Lo Monaco, S. (2004): Geochemical implications of trace elements and sulfur in the saturate, aromatic and resin fractions of crude oil from the Mara and Mara oeste fields, Venezuela. *Fuel*, 83 (3), pp 365-374.
- [51] López, L., Lo Monaco, S., Galarraga, F., Lira, A. & Cruz, C. (1995): V/Ni ratio in maltene and asphaltene fractions of crude oils from the west Venezuelan basin: correlation studies. *Chemical Geology*, 119 (1-4), pp 255-262.
- [52] Tribouillard, N., Algeo, T.J., Timothy Lyons, T. & Riboulleau, A. (2006): Trace metals as paleoredox and paleoproductivity proxies: an update. *Chemical Geology*, 232, pp 12-32.
- [53] Wehrli, B. & Stumm, W. (1989): Vanadyl in natural waters: adsorption and hydrolysis promote oxygenation. *Geochimica et Cosmochimica Acta*, 53, pp 69-77.
- [54] Sia, S.G. & Abdullah, W.H. (2011): Concentration and association of minor and trace elements in mukah coal from Sarawak, Malaysia, with emphasis on the potentially hazardous elements. *Int. J. Coal. Geol.* 88 (4), pp 179-193.
- [55] Huggins, F.E., Seidu, L.B.A., Shah, N., Huffman, G.P., Honaker, R.Q., Kyger, J.R., Higgins, B.L., Robertson, J.D., Pal, S. & Seehra, M.A. (2009): Elemental modes of occurrence in an Illinois #6 coal and fractions prepared by physical separation techniques at a coal

- preparation plant. *International Journal of Coal Geology*, 78 (1), pp 65-76.
- [56] Coveney, R.M., Jr., Murowchick, J.B., Grauch, R.I., Glascock, M.D. & Denison, J.R. (1992): Gold and platinum in shales with evidence against extra-terrestrial sources of metals: *Chemical Geology*, 99 (1-3), pp. 101-114.
- [57] Hatch, J.R., & Leventhal, J.S. (1992): Relationship between inferred redox potential of the depositional environment and geochemistry of the Upper Pennsylvanian (Missourian) Stark Shale Member of the Dennis Limestone, Wabaunsee County, Kansas, U.S.A.: *Chemical Geology*, 99 (1-3), pp. 65-82.
- [58] Piper, D.Z. (1999): Trace elements and major-element oxides in the Phosphoria Formation at Enoch Valley, Idaho—Permian sources and current reactivities: *U.S. Geological Survey Open-File Report*, 99-163, 66 p.
- [59] Vine, J.D. & Tourtelot, E. (1970): Geochemistry of black shale deposits – a summary report. *Economic Geology*, 65 (3), pp 253-272.
- [60] Love, J.D., Smith, L.E., Browne, D.G., and Carter, L.M., 2003, Vanadium deposits in the Lower Permian Phosphoria Formation, Afton area, Lincoln County, western Wyoming: *U.S. Geological Survey Professional Paper*, 1637, 28 p.,
- [61] Coveney, R.M., Jr., Leventhal, J.S., Glascock, M.D., & Hatch, J.R. (1987): Origins of metals and organic matter in the Mecca Quarry Shale Member and stratigraphically equivalent beds across the Midwest: *Economic Geology*, 82, pp. 915-933.
- [62] Pelletier, R.A. (1930): The zinc, lead and vanadium deposit of broken hill, N.Rhodesia. *S. Afr. Min. Eng*, 40, 91.
- [63] Gomes, H.I., Jones, A., Rogerson, M., Burke, I.T. & Mayes, W.M. (2016): Vanadium removal and recovery from bauxite residue leachates by ion exchange. *Environmental Science and Pollution Research*, 23, pp 23035-23042.
- [64] Abed, M.A., Saffarini, G.A. & Sadaqah, R.M. (2014): Spatial distribution of uranium and vanadium in the upper phosphorite

- member in Eshidiyya basin, southern Jordan. *Arab Journal of Geoscience*, 7, pp 253-271.
- [65] Judd, J.C., Sandberg, R.G. & Huiatt, J.L. (1986): Recovery of vanadium, uranium and phosphate from Idaho phosphorite ores. *U.S. Bureau of Mines Report of Investigations 9025*, pp 1-15.
- [66] Teng, Y., Ni, S., Zhang, C., Wang, J., Lin, X. & Huangm Y/ (2006): Environmental geochemistry and ecological risk of vanadium pollution in Panzhihua mining and smelting area, Sichuan, China. *Chinese journal of geochemistry*, 25(4), pp 379-385.
- [67] Zhang, G-Q., Zhang, T-A., Lu, G-Z., Zhang, Y., Liu, Y. & Liu, Z-L/ (2015): Extraction of vanadium from vanadium slag by high pressure oxidative acid leaching. *International Journal of Minerals, Metallurgy and Materials*, 22 (1), pp 21-26.
- [68] Notebaart, C.W. and Korowki, S.P. (1980): Famous mineral localities: The Broken Hill mine (Zambia). *Mineralogical Record*, 11(6), pp 339-348.
- [69] Kamona, A.F. and Friedrich, G.H. (2007): Geology, mineralogy and stable isotope geochemistry of the Kabwe carbonate-hosted Pb-Zn deposit, Central Zambia. *Ore Geology Reviews*, 30, pp 217-243.
- [70] Praszkiar, T. (2013) Mibladen, Morocco. *Mineralogical Record*, 44, pp. 247-285.
- [71] Howard, J.M and Owens, D.R (1995). *Rocks and Minerals*, 70, pp. 154-170.